Supporting Information

Modulating rheological properties of supramolecular networks by pH-responsive double-axle intrusion into γ-cyclodextrin

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1. Synthesis of PEG−b−PEI−g−dextran (PEG−PEI−dex)

PEG monotosylate (PEGOTs): colourless oil, TLC: 10% v/v MeOH in CHCl₃, Rₜ = 0.37; Flash column chromatography: silica gel 70-230, eluent; gradient 0–10% v/v MeOH in CHCl₃; δₜ (300 MHz, CDCl₃, Me₄Si) 7.81 and 7.25 (4H, d, Ph), 4.17 (2H, t, CH₂OTs), 3.62 (4H × 12, m, CH₃CH₂O), 2.43 (3H, s, Me).

PEG−b−POz copolymer (PEG−POz): pale yellow oil, ν_max(NaCl)/cm⁻¹ 3444 (OH), 3333 (NH), 1644 (CO), 1541 (NH) and 1064 (OH); δₜ (300MHz, CDCl₃, Me₄Si) 3.58 (4H × 12, m, CH₃CH₂O), 3.40 (4H × 14, s, CH₂CH₂N), 2.40 (2H, m, COCH₂CH₃), 0.93 (3H, m, COCH₂CH₃); δₜ (75.5 MHz, CDCl₃) 173.8 (1, d, NCO), 71.8 (1, OCH₂CH₂OH), 70.0-69.8 (2, CH₂CH₂O), 67.9 (1, OCH₂CH₂N) 60.8 (1, CH₂OH), 44.7 (2, CH₂CH₂N), 42.5 (1, CH₃NH₂) 25.2 (1, COCH₂CH₃), 8.7 (1, COCH₂CH₃).

PEG−b−PEI copolymer (PEG−PEI): pale yellow powder, ν_max(KBr)/cm⁻¹ 3333 (NH), 1712 (CO) and 1523 (NH); δₜ (300 MHz, D₂O at 80 °C) 3.58 (4H × 12, m, CH₃CH₂O), 3.23 (4H × 14, s, CH₂CH₂NH); δₜ (75.5 MHz, D₂O at 80 °C) 177.1 (1, COOH), 70.1 (2 × 12, CH₃CH₂O), 48.3 (2 × 14, CH₂CH₂N), 34.5 (1, CH₂COOH).

PEG−b−PEI−g−dextran (PEG−PEI−dex): yellow powder, δₜ (300 MHz, DMSO-d₆) 4.81 (1H × 328, d, Cₐ of dextran ), 3.59-3.11 (4H × 328, Cₐ, C₈ and C₆ of dextran) 3.53 (4H × 12, CH₃CH₂O), 3.45 (4H × 14 , CH₂CH₂N), 3.41-3.31 (2H × 328, C₂ and C₆ of dextran).
Scheme S1. Synthetic route for the PEG–PEI–dex.

Figure S1. $^1$H NMR spectrum of PEGOTs in CDCl$_3$, at 25 °C.
Figure S2. $^1$H NMR spectrum of PEG–POz in CDCl$_3$ at 25 °C.

Figure S3. $^1$H NMR (300 MHz) spectrum of PEG–PEI in D$_2$O at 80 °C.
Figure S4. GPC traces of PEG (green), PEGOTs (blue), and PEG–POz (red).

Table S1. Molecular weight data of polymers

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<th>DP</th>
<th>NMR</th>
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<td></td>
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<td></td>
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<td>$M_n$ (ml/g)</td>
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<td>PEG-POz</td>
<td>13 : 54</td>
<td>6 000</td>
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<tr>
<td>PEG600</td>
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Figure S5. $^1$H NMR (300 MHz) spectrum of PEG–PEI–dex in D$_2$O at 25 °C.

2. Viscoelasticity of the supramolecular network between PEG–PEI–dex and γ-CD

Figure S6. The viscosity curve and shear stress vs. shear rate of PEG–PEI–dex-γ-CD.
3. Dynamic light scattering (DLS) study of the supramolecular network between PEG–PEI–dex and γ-CD

**Instruments.** DLS measurements were carried out using Zetasizer Nano ZS (ZEN 3600, Malvern Instruments). The wavelength and scattering angle of laser were 633 nm and 90°, respectively. The size distribution was calculated from the intensity autocorrelation functions that were analyzed using CONTIN method. All measurements were controlled at room temperature.

**Sample preparation.** γ-CD (Kanto Chemical Co., Japan) was dissolved in boiling distilled water and recrystallized twice and dried in vacuo at 120 °C for 6 h before use. Samples for measurement were diluted to the designated concentrations at the range from 0.5 to 10 mg/mL and ultimately filtered through 0.2 µm filter. The PEG–PEI–dex solutions were prepared as the same manner. For the formation of supramolecular network, the pre-weighted solutions of γ-CD and PEG–PEI–dex was mixed and stirred at room temperature, followed by adjusting pH to 10 or 4.

**The size distribution of samples.** It was reported that the aqueous solution of CDs exhibits bimodal distribution with two kinds of size in terms of hydrodynamic radius by DLS measurement\(^1\). In our case, the aqueous solution of γ-CD exhibited a bimodal distribution containing one less than 1 nm and the other around 100 nm, assigned the small size to the monomeric γ-CD and the large size to the self-aggregated γ-CD, respectively as shown in Figure S7. For the PEG–PEI–dex solution, single size distribution was observed at around 8 nm when the solution was treated with 0.2 µm filter. For the inclusion complex at pH 10, a different peak from each peak in γ-CD and PEG–PEI–dex solution was observed at around 20 nm, indicating the presence of supramolecular structures by inclusion complexation. For the inclusion complex at pH 4, the peak assigned to supramolecular structures was observed at larger size than one at pH 10. This result suggests that the supramolecular structure was transformed to looser structure by chaining pH from pH 10 to 4.

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Figure S7. Size distribution data by DLS measurement for aqueous solutions of (a) γ-CD (green line) and PEG–PEI–dex (red line), and (b) PEG–PEI–dex–γ-CD at pH 10 (green line) PEG–PEI–dex–γ-CD at pH 4 (red line). Concentration of solutions: [γ-CD] and [PEG–PEI–dex] = 1.0 mg/ml, [PEG–PEI–dex–γ-CD] = 2.0 mg/ml.